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LAUNDRY-AID COMPOSITION

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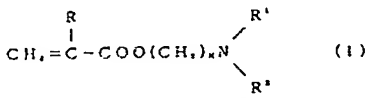
[There are no amendments to this patent.]

Claim

1. A laundry-aid composition, characterized by the fact that it is coated with a mixture consisting of a copolymer containing

(A) at least one basic monomer shown by general formula (I)



(I)

(where R is hydrogen or a methyl group, R^1 and R^2 are C_{1-3} alkyl groups, and x is an integer between 1 and 4),

(B) at least one water-insoluble or difficultly water-soluble monomer,

(C) at least one water-soluble monomer,

and at least one compound selected from a water-insoluble or difficultly water-soluble inorganic compound and a water-soluble or water-swollen nonionic polymer compound.

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Detailed explanation of the invention

Industrial utilization field

The present invention relates to a laundry-aid composition. In particular, it relates to a laundry-aid composition that can be used together with an alkaline detergent.

Conventional technology

In general, the washing cycle in a washing machine consists of water introduction, washing, dewatering, rinsing, and dewatering. In order to enhance the effect of laundry aids, such as softening-finishing agents, in a perfect manner, they have been added after the completion of washing. Conventionally, housewives generally operate the various steps in sequence in the washing machine. In this case, after the completion of the washing step with the addition of a detergent beforehand, the addition of laundry aids, such as a softener, a bleaching agent, and a paste, in the rinsing step is not a burden or a major hindrance. However, with the recent popularization of semiautomatic and completely automatic washing machines, housewives have been able to eliminate the intermediate operations. However, these operations have not been completely eliminated since there is an operation involving the addition of a laundry aid.

In blending a laundry aid in a detergent composition for use, the effective ingredients are protected during washing. They are absorbed onto clothes and are transferred to the rinsing

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step. It is necessary that the effective ingredients are leached into the rinsing solution at the same time as the initiation of rinsing.

Problems to be solved by the invention

If a laundry aid is coated with a polymer that is practically insoluble in an alkaline washing solution and is soluble in a neutral rinsing solution, the laundry-aid ingredients are protected from the alkaline washing solution during washing. During the rinsing step, the laundry-aid ingredients can be leached into the rinsing solution. In doing this, the effectiveness of the aid can be efficiently enhanced. At the same time, since the laundry aids that have to be added in the rinsing step conventionally are blended effectively right from the beginning, the time needed for the laundry-aid addition can be spared.

Several polymers whose solubilities vary with the pH have been conventionally known. For example, polyvinyl acetal diethylaminoacetate is insoluble in water in the neutral range. However, it is dissolved in water in the acidic range, starting at pH 5.8. Furthermore, the copolymer of vinylpyridine and acrylic acid is dissolved in water at a pH less than 4 and a pH higher than 7.4. It is insoluble in water in a pH range between these two. However, polymers that are insoluble in alkaline water, soluble in essentially neutral or acidic water, and that have varied solubilities in a narrow pH range have not been known

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to date. The present applicant has proposed copolymers like these or laundry aids coated with these in Japanese Patent Application No. Sho 58[1983]-247997.

However, for the laundry aids coated with this copolymer, further improvements have been made in regard to the adsorption with respect to cotton cloth. In the case of washing cotton underwear or the like, there are many laundry aids that are not adsorbed in cotton cloths and are discharged together with the washing solution after washing out of the washing-bath tank. The effectiveness of the laundry-aid addition cannot be sufficiently enhanced.

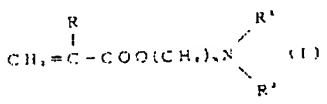
Means to solve the problems

The objective of the present invention is to provide a laundry aid that can be protected in a stable manner in an alkaline washing solution, adsorbed sufficiently onto cotton cloth, in particular, transferred into the rinsing step, and that can enhance the effectiveness of the neutral rinsing solution.

In other words, the laundry aid of the present invention is characterized by the fact that it is coated with a mixture containing component (a) and component (b) shown in the following.

(a) a copolymer containing the following three monomers (A), (B), and (C)

(A) at least one of the basic monomers represented by general formula I,



(I)

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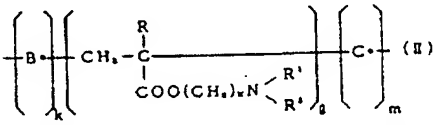
(where R is hydrogen or a methyl group, R^1 and R^2 are C_{1-3} alkyl groups, and x is an integer between 1 and 4),

(B) at least one water-insoluble or difficultly water-soluble monomer,

(C) at least one water-soluble monomer,

(b) at least one compound selected from a water-insoluble or difficultly water-soluble inorganic compound and a water-soluble or water-swollen nonionic polymer compound.

The copolymer of component (a) mentioned previously is practically insoluble in an alkaline aqueous solution and is soluble in a neutral or acidic aqueous solution. However, it is preferable that, as a laundry aid, this is insoluble in alkaline water at a pH above about 9.5 and soluble in slightly alkaline or acidic water under a pH of about 8.5, and that it has a high solubility ratio in the presence of a surfactant. From this viewpoint, the copolymerization ratio of copolymer (a) is properly in the range of k/(k + l + m) = 0.05 to 0.8 and l/(k + l + m) = 0.05 to 0.8, preferably k/(k + l + m) = 0.05 to 0.6 and l/(k + l + m) = 0.1 to 0.7, in general formula (II).



(where B* and C* represent the constituent units derived from monomers (B) and (C), respectively). Furthermore, the degree of polymerization k + l + m is properly 100 to 50,000, preferably 300 to 20,000.

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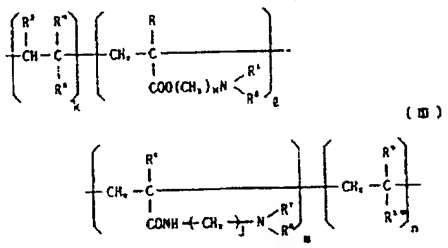
As a compositional example of a proper copolymer, that represented by the following general formula (III) can be mentioned.



(III)

where R is H or CH_3

R^1 is a C_1 to C_3 alkyl group

R^2 is a C_1 to C_3 alkyl group

x is an integer between 1 and 4

R^3 is H or a C_1 to C_4 alkyl group

R^4 is H or a C_1 to C_4 alkyl group or $-COOR^{11}$ (where R^{11} is a C_1 to C_{18} alkyl group)

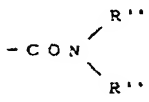
R^5 is $-COOR^{12}$, $-OCOR^{12}$ (where R^{12} is a C_1 to C_{18} alkyl group, or $-C_6H_5$

R^6 is H or a C_1 to C_4 alkyl group

R^7 and R^8 are the same or different and are C_1 to C_4 alkyl groups

J is an integer between 1 and 4

R^9 is H or a C_1 to C_4 alkyl group

R^{10} is $-OH$, $-CN$, $-(CH_2)_yOH$ (where y = 1 to 4), 

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(where R^{13} and R^{14} are the same or different and may be H or C_1 to C_{18} alkyl groups), $-COO(CH_2CH_2O)pH$, or $-COO(CH_2CH_2)pCH_3$ (where p = 1 to 30)

$k/(k + l + m + n) = 0.05$ to 0.8

$l/(k + l + m + n) = 0.05$ to 0.8

$m/(k + l + m + n) = 0.05$ to 0.8

$n/(k + l + m + n) = 0$ to 0.5

The preferred copolymers among these can be classified as the case ($n \neq 0$) containing the 4th component and the case essentially containing no 4th component, as shown in the following:

(1) Case containing the 4th component

R is H or $-CH_3$

R^1 is $-CH_3$ or $-C_2H_5$

R^2 is $-CH_3$ or $-C_2H_5$

R^3 is H

R^4 is H, $-CH_3$, $-COOR^{11}$ (R^{11} is a C_1 to C_8 alkyl group)

R^5 is $-COOR^{12}$ (where R^{12} is a C_1 to C_8 alkyl group) or $-OCOCH_3$

R^6 is H or $-CH_3$

R^7 and R^8 are $-CH_3$ and $-C_2H_5$

J is 1 to 4

R^9 is H or $-CH_3$

R^{10} is $-COO(CH_2CH_2O)pH$ (where p = 1 to 5), $-COO(CH_2CH_2O)pCH_3$ (where p = 1 to 5), $-CON(CH_3)_2$, or $-CON(C_2H_5)_2$

$k/(k + l + m + n) = 0.05$ to 0.5

$l/(k + l + m + n) = 0.1$ to 0.65

$m/(k + l + m + n) = 0.1$ to 0.6

$n/(k + l + m + n) = 0.01$ to 0.5

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(2) Case essentially containing no 4th component (n = 0)

R is H or $-CH_3$

R^1 is $-CH_3$ or $-C_2H_5$

R^2 is $-CH_3$ or $-C_2H_5$

R^3 is H

R^4 is H, $-CH_3$, $-COOR^{11}$ (R^{11} is a C_1 to C_8 alkyl group)

R^5 is $-COOR^{12}$ (where R^{12} is a C_1 to C_8 alkyl group) or $-OCOCH_3$

R^6 is H or $-CH_3$

R^7 and R^8 are $-CH_3$, $-C_2H_5$

J is 1 to 4

k/(k + l + m) = 0.05 to 0.6

l/(k + l + m) = 0.1 to 0.7

m/(k + l + m) = 0.1 to 0.7

Specific examples of the various monomer components (A), (B), and (C) are shown in the following:

The basic monomers (the second component of general formula III) shown in general formula (I) in (A) mentioned previously are the major monomer components needed in order to obtain pH-responsive copolymers that can be used in the present invention. N,N-dimethylaminoethyl acrylate, N,N-dimethylaminomethyl acrylate, N,N-dimethylaminobutyl acrylate, N,N-dimethylaminopropyl acrylate, N,N-dimethylaminoethyl methacrylate, N,N-dimethylaminomethyl methacrylate, N,N-dimethylaminobutyl methacrylate, N,N-dimethylaminopropyl methacrylate, N,N-diethylaminoethyl acrylate, N,N-diethylaminomethyl acrylate, N,N-diethylaminobutyl acrylate, N,N-diethylaminopropyl acrylate, N,N-diethylaminoethyl methacrylate, N,N-diethylaminomethyl methacrylate, N,N-diethylaminobutyl

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methacrylate, N,N-diethylaminopropyl methacrylate, and so on can be exemplified. These may be used alone or in combinations of two or more.

The water-insoluble or difficultly water-soluble monomers (the first component of general formula III) in (B) are the components that contribute to the broadening of the insoluble pH range of the pH-responsive copolymers. As specific examples, one or more selected from acrylic acid esters, methacrylic acid esters, crotonic acid esters, itaconic acid esters, vinyl acetate, and styrene can be mentioned. If the various alkyl esters of acrylic acid, methacrylic acid, crotonic acid, and itaconic acid are used as monomers (B), those with a carbon chain length of 1 to 18 in the alkyl group with the ester bond can be used. If the alkyl chain is too long, the dissolution of the resulting copolymer in the slightly alkaline aqueous solution will be slow. It is preferable that the number of carbon atoms in these alkyl groups is 1 to 8. Methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, and so on are especially preferred typical examples.

The water-soluble monomers (the third and fourth components of general formula III) in (C) are the components that contribute to the broadening of the soluble pH range of the pH-responsive copolymers. As specific examples, one or more selected from N,N-dimethylaminopropyl acrylic acid (or methacrylic acid) amide, N,N-dimethylaminomethyl acrylic acid (or methacrylic acid) amide, N,N-dimethylaminoethyl acrylic acid (or methacrylic acid) amide, N,N-dimethylaminobutyl acrylic acid (or methacrylic acid) amide, N,N-dimethylamino acrylic acid (or methacrylic acid) amide, 2-

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hydroxyethyl acrylic acid (or methacrylic acid), 2-hydroxypropyl acrylic acid (or methacrylic acid), or an ester of polyethylene glycol or methoxy polyethylene glycol (the average number of mol added p = 1 to 30 for ethylene glycol in any case) and acrylic acid or methacrylic acid can be mentioned.

The copolymers that can be used in the present invention can be obtained by ordinary radical polymerization under atmospheric pressure or increased pressure. Acetone or the like may be used as a polymerization solvent, and azobisisobutyronitrile or the like may be used as a polymerization initiator.

The polymerization temperature and time vary with the polymerization solvent used and the composition of the monomer. In general, 40 to 90°C and 5 to 20 h are appropriate.

As component (b) of the coating mixture used for the coating of a laundry aid, a water-insoluble or difficultly water-soluble inorganic compound or a water-soluble or water-swollen nonionic polymer compound is used.

The water-insoluble or difficultly water-soluble inorganic compound in component (b) is a compound with a solubility of less than 0.5 with respect to water. As specific examples, calcium carbonate, barium carbonate, magnesium carbonate, magnesium calcium carbonate, calcium carbonate, barium carbonate [sic; parium calcium carbonate], silicon oxide, titanium oxide, aluminum silicate, calcium phosphate, and so on can be mentioned. Among these, calcium carbonate, barium carbonate, and titanium oxide are preferred.

Furthermore, as the nonionic polymer of component (b), polyvinyl alcohol, polyvinylpyrrolidone, polyacrylamide, hydroxypropylcellulose, hydroxyethylcellulose,

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hydroxypropylmethylcellulose, methylcellulose, alginic acid propylene ester, dextran, pullulan, the bacterial surface polysacchardie of Pullularia pullulans, and lepan [transliteration] can be exemplified. Among these, polyvinyl alcohol and polyacrylamide are preferred. Polyvinyl alcohol with a different degree of saponification can be used. However, one with a degree of saponification of 80 to 90 mol% is preferably used.

The laundry aid is coated with a mixture of component (a) and component (b). At this time, it is preferable that component (b) is present in this coating mixture as particles. If the water-insoluble or difficultly water-soluble inorganic compound is used as component (b), its proper particle diameter is 0.01 to 300 μm, preferably 0.01 to 150 μm. Furthermore, it is proper to use a nonionic polymer compound with a particle size of 1 to 300 μm, preferably 10 to 150 μm. If the particle diameter is too large, it will be a nonuniform dispersion and the effectiveness in improving the degree of adsorption will decrease.

The proper ratio of component (a) and component (b) in the coating mixture is 1 to 100 parts by weight, preferably 5 to 50 parts, of (b) water-insoluble or difficultly water-soluble inorganic compound or nonionic polymer compound with respect to 100 parts by weight of copolymer (a).

As the laundry aids to be coated, a long-chained dialkldimethylammonium salt, 1-methyl-1-long-chained alkanoylaminoethyl-2-long-chained alkyl imidazolinium salt, long-chained dialkyldimethylammonium salt, fatty acid salt mixtures, and other softening-finishing agents, silicone oils and other

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defoaming agents, hypochlorite, percarbonate, organic peracids, and other bleaching agents, pastes, blue-tint-rendering agents, fluorescent whiteners, enzymes, and so on are available.

In the manufacture of a laundry aid of the present invention, for example, copolymer (a) is dissolved at 1 to 20 wt% in a solvent selected according to the type of laundry aid, as shown in the following. Next, particles of the water-insoluble or difficultly water-soluble inorganic compound or water-soluble nonionic polymer in component (b) are dispersed to prepare a coating-agent solution.

Softening-finishing agents: acetone, methanol, ethanol, acetone-water, ethanol-water, methanol-water

Defoaming agents: acetone, methanol, ethanol, acetone-water, ethanol-water, methanol-water

Pastes: acetone, methanol, ethanol, isopropyl alcohol, chloroform

Bleaching agents: acetone, methanol, ethanol, isopropyl alcohol

Perfumes and blue-tint-rendering agents: water-acetone, water-methanol, water-ethanol

Fluorescent whiteners and enzymes: acetone, methanol, ethanol, isopropyl alcohol, chloroform

Next, the laundry aids prepared beforehand are coated by spraying the coating agent solution in a pan or a fluidized bed. It is proper that the coated laundry aids obtained in this manner are prepared so that the particle diameter is 50 to 500 μm. Furthermore, the coating is appropriate when the coating amount is 5 to 50 wt% of the laundry-aid particles.

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Furthermore, after the mixture of component (a) and component (b) used for the laundry aid has been granulated, this may be further coated with a mixture of component (a) and component (b). In doing this, the adjustment of the particle size of the laundry aid obtained is facilitated.

Effects

According to the present invention, by coating a laundry aid with a mixture containing copolymer (a) that is pH-responsive, the laundry aid is protected in an alkaline washing solution, and is leached and activated in a rinsing solution. At this time, the water-insoluble or difficultly water-soluble compound, or the water-insoluble nonionic polymer compound, of component (b) is contained in the coating mixture. In doing this, the degree of adsorption onto clothes, especially cotton cloth, is improved during washing. Many laundry aids are efficiently transferred from the washing step to the rinsing step. In the rinsing step, their power is effectively exhibited.

Thus, the laundry-aid composition of the present invention is one that exhibits its effectiveness by the addition into a granular detergent containing an anionic surfactant, in particular. It is convenient to blend this in the detergent beforehand. Of course, this may be stored separately from the detergent composition. This may be added individually into the washing solution during washing. Furthermore, this can be used alone without combining with the detergent.

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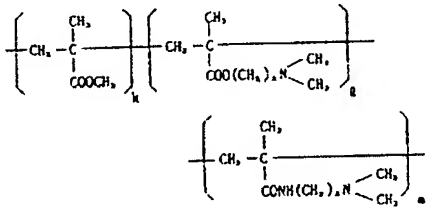
Effectiveness

According to the present invention, the effective ingredients of the laundry aids are protected in the washing solution. Furthermore, since the degree of adsorption onto cotton cloth is high, it is adsorbed onto clothes and effectively transferred to the rinsing step. By the leaching of the effective ingredients here, a high laundry-aid effectiveness can be obtained by the addition of a small amount.

Application examples

Application Example 1

Calcium carbonate powder (particle diameter of 20 to 100 μm) and a copolymer with the following structure were subjected to acetone dispersion and dissolution at a weight ratio of 1 to 5, so that the total concentration was 5 wt%. To this, an oil-soluble dye, Blue Dye No. 403, was added at 0.3 wt% with respect to solids to prepare a coating agent solution.



$(k/(k + l + m) = 0.35,\ l/(k + l + m) = 0.45,$
and $k + l + m = 800$ to $1,400)$.

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Next, 44 parts by weight of distearyldimethylammonium chloride powder (350 to 500 μm) were placed in a pan and the previously mentioned coating-agent solution was sprayed. Coating was carried out so that the coating agent was coated at 10 wt%, calculated based on the solids, to form a blue laundry aid. Two parts by weight of the laundry aid obtained in this manner and 98 parts by weight of a commercial detergent A (a heavy detergent with a straight-chained alkylbenzenesulfonic acid sodium salt as a major component) were mixed. A total of 6.7 g was added into a commercial Mini-Mini [possibly a brand name] washing machine (amount of water 5 L). One cotton underwear item (half sleeve) was washed for 10 min. Next, the item was removed from the bath tank and dewatered. The number of laundry-aid particles (blue) adsorbed onto the cloth was examined. The results are shown in Table I later.

Application Example 2

44 parts by weight of distearyldimethylammonium chloride powder (350 to 500 μm), 5 parts by weight of silica powder, and 51 parts by weight of a 40-wt% acetone solution of the copolymer used in Application Example 1 were mixed. The acetone was removed under reduced pressure. It was pulverized and prepared at a particle size of 350 to 500 μm using sieves. Next, these particles were placed in a pan and the same coating agent solution as in Application Example 1 was sprayed. A blue laundry aid was obtained, such that the coating agent was coated at 10 wt%, calculated as solids.

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The number of adsorbed particles was examined after washing in the same manner as in Application Example 1, except that the laundry aid obtained in this manner was used.

Application Example 3

A laundry aid was obtained in the same manner as in Application Example 1, except that polyvinyl alcohol (degree of saponification 87%, particle diameter 20 to 50 μm) was used at the same amount instead of the calcium carbonate used in Application Example 1. The number of adsorbed particles was examined.

Comparative Example 1

A laundry aid was prepared in the same manner as in Application Example 1, except that one containing no calcium carbonate powder was used as the coating-agent solution in Application Example 1. The number of adsorbed particles was examined.

For those mentioned previously, the number of laundry-aid particles adsorbed onto the cotton underwear are shown in Table I as relative values (adsorption efficiencies) with 100 used as the case of Comparative Example 1.

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Table I.

	Absorption efficiency
Application Example 1	145
Application Example 2	145
Application Example 3	150
Comparative Example 1	100

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